

# **STIC Search Report**

## **Biotech-Chem Library**

STIC Database Tracking Number: 148073

TO: Rei-Tsang Shiao  
Location: 5a10 / 5c18  
Thursday, March 24, 2005  
Art Unit: 1626  
Phone: 571-272-0707  
Serial Number: 10 / 6536~~18~~ 88

From: Jan Delaval  
Location: Biotech-Chem Library  
Remsen 1a51  
Phone: 571-272-22504  
[jan.delaval@uspto.gov](mailto:jan.delaval@uspto.gov)

### Search Notes

# SEARCH REQUEST FORM

Scientific and Technical Information Center

Requester's Full Name: Robert (Rettig) Shiao Examiner #: 79521 Date: 3/17/05  
 Art Unit: 1626 Phone Number: 2-0107 Serial Number: 19653, 688  
 Mail Box and Bldg/Room Location: 5A10/sc 18 Results Format Preferred (circle): PAPER DISK E-MAIL

If more than one search is submitted, please prioritize searches in order of need.

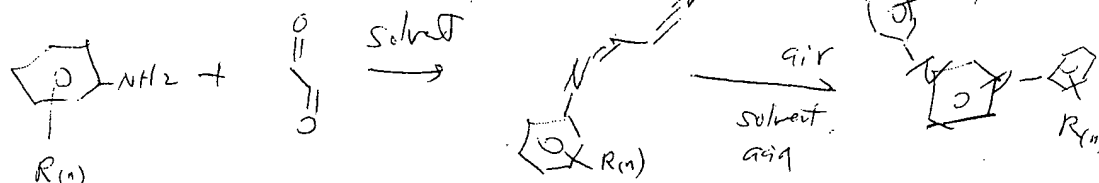
Please provide a detailed statement of the search topic, and describe as specifically as possible the subject matter to be searched. Include the elected species or structures, keywords, synonyms, acronyms, and registry numbers, and combine with the concept or utility of the invention. Define any terms that may have a special meaning. Give examples or relevant citations, authors, etc., if known. Please attach a copy of the cover sheet, pertinent claims, and abstract.

Title of invention: Synthesis of 1,3-disubstituted  
 Inventors (please provide full names): Nolan

Earliest Priority Filing Date: \_\_\_\_\_

\*For Sequence Searches Only\* Please include all pertinent information (parent, child, divisional, or issued patent numbers) along with the appropriate serial number.

2. Search a process for making imidazolin salt  
 by: (see Diagram D) see claim 1, 2/18



\* R is sub, i.e.  
 alkyl

## STAFF USE ONLY

Searcher: <u>Am</u>	Type of Search	Vendors and cost where applicable
Searcher Phone #: <u>22604</u>	NA Sequence (#) _____	STN <input checked="" type="checkbox"/>
Searcher Location: _____	AA Sequence (#) _____	Dialog _____
Date Searcher Picked Up: <u>3/24/05</u>	Structure (#) <input checked="" type="checkbox"/>	Questel/Orbit _____
Date Completed: <u>3/24/05</u>	Bibliographic _____	Dr. Link _____
Searcher Prep: Review Time _____	Litigation _____	Lexis/Nexis _____
Clerical Prep: me: <u>15</u>	Fulltext _____	Sequence Systems _____
Online Time: <u>445</u>	Patent Family _____	WWW/Internet _____
	Other _____	Other (specify) _____

=> d his

(FILE 'HCAPLUS' ENTERED AT 14:12:00 ON 24 MAR 2005)

DEL HIS  
E NOLAN S/AU  
L1 75 S E3,E8,E30,E32,E35,E37  
L2 5 S L1 AND ?IMIDAZOL?  
L3 1 S L2 AND 1 3 DISUBSTITUTED  
L4 11 S 1 3 BIS 2 6 DIISOPROPYLPHENYL IMIDAZOLIUM CHLORIDE  
L5 14 S 1 3 BIS 2 6 DIISOPROPYLPHENYL IMIDAZOLIUM?  
L6 2 S L2 AND ?DIISOPROPYL?  
L7 3 S L2 AND (1 3 OR 2 6)  
L8 1 S L3 AND L6,L7  
L9 3 S L6-L8  
L10 2 S L9 AND BIS  
SEL RN

FILE 'REGISTRY' ENTERED AT 15:01:24 ON 24 MAR 2005

L11 11 S E1-E11  
L12 1 S L11 AND NCNC2/ES AND CL  
L13 1 S 286014-24-2  
L14 10 S 286014-24-2/CRN  
L15 1 S L14 AND I  
L16 2 S L12,L15  
L17 1 S L11 AND C2H2O2  
L18 1 S L11 AND C12H19N  
L19 1 S L11 AND C26H36N2  
E PARAFORMALDEHYDE/CN  
L20 1 S E3  
E HYDROCHLORIC ACID/CN  
L21 1 S E3  
E BF4H/MF  
L22 1 S 14874-70-5  
E TETRAFLUOROBOR/CN  
E F6P/MF  
L23 3 S E3  
L24 7 S L11 NOT CCS/CI

FILE 'HCAPLUS' ENTERED AT 15:31:22 ON 24 MAR 2005

L25 695 S ?DIAZABUTADIEN?  
L26 0 S L1 AND L25

FILE 'REGISTRY' ENTERED AT 15:32:31 ON 24 MAR 2005

L27 5 S (METHANOL OR ETHYL ACETATE OR ETHANOL OR TETRAHYDROFURAN OR T  
E C20H24N2/MF  
L28 153 S E3 AND 46.150.18/RID AND 2/NR  
L29 3 S L28 AND BENZENAMINE AND ETHANEDIYLIDENE BIS  
L30 2 S L29 AND TRIMETHYL  
L31 1 S DIOXANE/CN  
L32 1554 S 123-91-1/CRN  
L33 5 S L32 AND CLH  
L34 2 S L33 AND 2/NC  
L35 3 S L11 AND NCNC2/ES NOT L12,L13  
L36 1 S L35 AND C27H36N2  
L37 1 S 244187-81-3/CRN  
L38 1 S METHANOL/CN  
L39 1 S ETHYL ACETATE/CN

FILE 'HCAPLUS' ENTERED AT 15:37:56 ON 24 MAR 2005

L40 6694 S L17  
L41 11213 S GLYOXAL  
L42 528 S ETHANEDIAL  
L43 18 S GLYOXAZAL

L44 36 S GLYOXYLALDEHYDE  
L45 12111 S L40-L44  
L46 33 S L30  
L47 61 S L16  
L48 4 S L45 AND L47  
L49 2 S L46 AND L47  
L50 2 S L48 AND L49  
L51 5 S L16 (L) PREP+NT/RL  
L52 3 S L51 AND L45,L46  
L53 1 S L1 AND L47  
L54 3 S L52,L53  
L55 0 S L54 AND L31,L34,L27  
L56 0 S L54 AND L20-L23  
L57 0 S L54 AND L27  
L58 2 S L37  
L59 0 S L37(L) PREP/RL  
L60 8 S L10,L54,L58,L51  
L61 3 S L60 AND (PY<=2002 OR PRY<=2002 OR AY<=2002)  
L62 4 S L10,L61

=> fil hcaplus

FILE 'HCAPLUS' ENTERED AT 15:43:53 ON 24 MAR 2005

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FILE COVERS 1907 - 24 Mar 2005 VOL 142 ISS 13

FILE LAST UPDATED: 23 Mar 2005 (20050323/ED)

This file contains CAS Registry Numbers for easy and accurate substance identification.

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L62 ANSWER 1 OF 4 HCAPLUS COPYRIGHT 2005 ACS on STN  
AN 2003:183602 HCAPLUS  
ED Entered STN: 11 Mar 2003  
TI Synthesis of 1,3-disubstituted  
imidazolium salts  
AU Kelly, Roy A., III; Sommer, William; Nolan, S. P.  
CS Department of Chemistry, University of New Orleans, New Orleans, LA,  
70148, USA  
SO Abstracts of Papers, 225th ACS National Meeting, New Orleans, LA, United  
States, March 23-27, 2003 (2003), INOR-559 Publisher: American Chemical  
Society, Washington, D. C.  
CODEN: 69DSA4  
DT Conference; Meeting Abstract  
LA English  
AB Imidazolium salts are the immediate precursors to N-heterocyclic  
carbenes (NHC) yet a simple, general synthetic route to a wide variety of  
imidazolium salt is not yet available. Such a straightforward

route is described for two specific members of this family of ligand precursor: **1,3-Bis(2,4,6-trimethylphenyl)imidazolium chloride** (IMes-HCl) and **1,3-Bis(2,6-diisopropylphenyl)imidazolium chloride** (IPr-HCl). The procedure appears general and similar protocols can be used to isolate various **imidazolium** salts. These and related NHC have been used in the synthesis of numerous palladium complexes. The general synthetic route to NHC precursors and the complexation to various metal centers will be discussed.

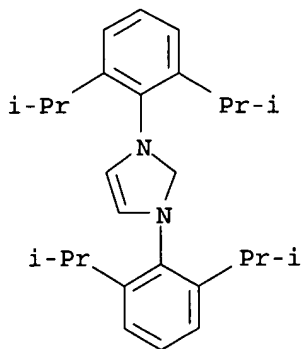
✓ L62 ANSWER 2 OF 4 HCAPLUS COPYRIGHT 2005 ACS on STN  
 AN 2000:656855 HCAPLUS  
 DN 133:362823  
 ED Entered STN: 20 Sep 2000  
 TI A sterically demanding nucleophilic carbene: **1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene**. Thermochemistry and catalytic application in olefin metathesis  
 AU Jafarpour, L.; Stevens, E. D.; Nolan, S. P.  
 CS Department of Chemistry, University of New Orleans, New Orleans, LA, 70148, USA  
 SO Journal of Organometallic Chemistry (2000), 606(1), 49-54  
 CODEN: JORCAI; ISSN: 0022-328X  
 PB Elsevier Science S.A.  
 DT Journal  
 LA English  
 CC 29-13 (Organometallic and Organometalloidal Compounds)  
 Section cross-reference(s): 75  
 OS CASREACT 133:362823  
 AB The sterically demanding nucleophilic carbene ligand **1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene** (IPr, 4) has been synthesized. The reaction of [Cp\*RuCl]<sub>4</sub> (5; Cp\* = η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>) with this ligand affords a coordinatively unsatd. Cp\*Ru(IPr)Cl (6) complex. Solution calorimetric results in this system provide information concerning the electron donor properties of the carbene ligand. Steric parameters associated with this ligand are determined from the x-ray crystal structure study. The carbene ligand reacts with RuCl<sub>2</sub>(:C(H)Ph)(PCy<sub>3</sub>)<sub>2</sub> to yield a mixed carbene-phosphine ruthenium complex RuCl<sub>2</sub>(:C(H)Ph)(IPr)(PCy<sub>3</sub>) (9). A single-crystal x-ray diffraction study has been performed on 9. The thermal stability of 9 has been studied at 60° and its catalytic activity has been evaluated for the ring closing metathesis of di-Et diallylmalonate.  
 ST sterically demanding nucleophilic carbene isopropylphenyl **imidazolylidene** ruthenium complex prepn; thermochem catalysis olefin metathesis isopropylphenyl **imidazolylidene** ruthenium complex; catalyst ring closing metathesis diallylmalonate isopropylphenyl **imidazolylidene** ruthenium complex; crystal mol structure isopropylphenyl **imidazolylidene** nucleophilic carbene ruthenium complex  
 IT Cyclization catalysts  
 (metathesis; preparation of sterically demanding nucleophilic carbene **bis(diisopropylphenyl)imidazolylidene** ruthenium complexes as)  
 IT Crystal structure  
 Molecular structure  
 (of sterically demanding nucleophilic carbene **bis(diisopropylphenyl)imidazolylidene** ruthenium complexes)  
 IT 3195-24-2, Diethyl diallylmalonate  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (**bis(diisopropylphenyl)imidazolylidene** ruthenium complex catalyzed ring closing metathesis of)

- IT 307519-47-7P  
RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation)  
(preparation and crystal structure of)
- IT 74663-75-5P  
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT  
(Reactant or reagent)  
(preparation and cyclization of)
- IT 250285-32-6P  
RL: RCT (Reactant); SPN (Synthetic preparation); PREP  
(Preparation); RACT (Reactant or reagent)  
(preparation and neutralization of)
- IT 244187-81-3P  
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT  
(Reactant or reagent)  
(preparation and reaction with ruthenium complexes)
- IT 21622-00-4P  
RL: SPN (Synthetic preparation); PREP (Preparation)  
(preparation of)
- IT 307519-48-8P  
RL: CAT (Catalyst use); PRP (Properties); SPN (Synthetic preparation);  
PREP (Preparation); USES (Uses)  
(preparation, crystal structure, and ring closing metathesis catalysis of  
diallylmalonate with)
- IT 113860-07-4, Tetrakis(chloro( $\eta^5$ -pentamethylcyclopentadienyl)ruthenium)  
172222-30-9, (Benzylidene)dichlorobis(tricyclohexylphosphine)ruthenium  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(reaction with bis(diisopropylphenyl)  
imidazolylidene as sterically demanding nucleophilic carbene)
- IT 107-22-2, Glyoxal  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(reaction with diisopropylaniline)
- IT 24544-04-5, 2,6-Diisopropylaniline  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(reaction with glyoxal)

RE.CNT 35 THERE ARE 35 CITED REFERENCES AVAILABLE FOR THIS RECORD  
RE

- (1) Ackermann, L; Tetrahedron Lett 1999, V40, P4787 HCAPLUS
- (2) Anon; private communication from AJ Arduengo III
- (3) Arduengo, A; US 5077414 1991 HCAPLUS
- (4) Arduengo, A; Chem Z 1998, V32, P6 HCAPLUS
- (5) Arduengo, A; J Am Chem Soc 1992, V114, P5530 HCAPLUS
- (6) Campion, B; J Chem Soc Chem Commun 1998, P278
- (7) Collman, J; Principles and Applications of Organotransition Metal  
Chemistry, 2nd 1987
- (8) Demonceau, A; Macromolecules 1997, V30, P3127 HCAPLUS
- (9) Diaz, E; J Am Chem Soc 1997, V119, P3887
- (10) Fagan, P; J Am Chem Soc 1998, V110, P2981
- (11) Herrmann, W; Angew Chem Int Ed Engl 1996, V35, P1087 HCAPLUS
- (12) Huang, J; J Am Chem Soc 1999, V121, P2674 HCAPLUS
- (13) Huang, J; Organometallics 1999, V18, P2370 HCAPLUS
- (14) Kilday, M; Res Natl Bur Stand (US) 1980, V85, P467 HCAPLUS
- (15) Kingsbury, J; J Am Chem Soc 1999, V121, P791 HCAPLUS
- (16) Lappert, M; J Organomet Chem 1988, V358, P185 HCAPLUS
- (17) Luo, L; Organometallics 1994, V13, P4781 HCAPLUS
- (18) Mohr, B; Organometallics 1996, V15, P4317 HCAPLUS
- (19) Nguyen, S; J Am Chem Soc 1992, V114, P3974 HCAPLUS
- (20) Nguyen, S; J Am Chem Soc 1993, V115, P9858 HCAPLUS
- (21) Nolan, S; Inorg Chem 1986, V25, P4446 HCAPLUS
- (22) Nolan, S; J Organomet Chem 1985, V282, P357 HCAPLUS
- (23) Ojelund, G; Acta Chem Scand 1968, V22, P1691
- (24) Parshall, G; Homogeneous Catalysis 1992
- (25) Perrin, D; Purification of Laboratory Chemicals 1988
- (26) Pignolet, L; Homogeneous Catalysis with Metal Phosphine Complexes 1983

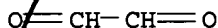
(27) Scholl, M; Tetrahedron Lett 1999, V40, P2247 HCAPLUS  
 (28) Schwab, P; Angew Chem Int Ed Engl 1995, V34, P2039 HCAPLUS  
 (29) Schwab, P; J Am Chem Soc 1996, V118, P100 HCAPLUS  
 (30) Serron, S; Organometallics 1998, V13, P534  
 (31) Stumpf, A; J Chem Soc Chem Commun 1995, P1127  
 (32) Ulman, M; Organometallics 1998, V17, P2484 HCAPLUS  
 (33) Wanzlick, H; Angew Chem Int Ed Engl 1962, V1, P75  
 (34) Wu, Z; J Am Chem Soc 1995, V117, P5503 HCAPLUS  
 (35) Yang, K; Organometallics 1997, V16, P5234 HCAPLUS  
 IT 250285-32-6P  
 RL: RCT (Reactant); **SPN (Synthetic preparation); PREP (Preparation)**; RACT (Reactant or reagent)  
 (preparation and neutralization of)  
 RN 250285-32-6 HCAPLUS  
 CN 1H-Imidazolium, 1,3-bis[2,6-bis(1-methylethyl)phenyl]-, chloride (9CI)  
 (CA INDEX NAME)



● Cl<sup>-</sup>

ONE OR MORE TAUTOMERIC DOUBLE BONDS NOT DISPLAYED IN THE STRUCTURE

IT 107-22-2, Glyoxal  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (reaction with diisopropylaniline)  
 RN 107-22-2 HCAPLUS  
 CN Ethanedial (9CI) (CA INDEX NAME)



✓ L62 ANSWER 3 OF 4 HCAPLUS COPYRIGHT 2005 ACS on STN  
 AN 1999:798077 HCAPLUS  
 DN 132:151738  
 ED Entered STN: 19 Dec 1999  
 TI Imidazolylidenes, imidazolinylidenes and imidazolidines  
 AU Arduengo, Anthony J., III; Krafczyk, Roland; Schmutzler, Reinhard; Craig, Hugh A.; Goerlich, Jens R.; Marshall, William J.; Unverzagt, Markus  
 CS Institut für Anorganische und Analytische Chemie, der Technischen Universität - Carolo Wilhelmina, Braunschweig, D-38106, Germany  
 SO Tetrahedron (1999), 55(51), 14523-14534  
 CODEN: TETRAB; ISSN: 0040-4020  
 PB Elsevier Science Ltd.  
 DT Journal  
 LA English

CC 28-9 (Heterocyclic Compounds (More Than One Hetero Atom))  
OS CASREACT 132:151738  
AB Starting from **glyoxal** and RNH<sub>2</sub> [R = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>,  
2,6-(Me<sub>2</sub>CH)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>], the corresponding 1,3-diarylimidazolinium chlorides  
were obtained in a 3-step sequence via diimines and ethylenediamine  
dihydrochlorides. Subsequent reduction with LiAlH<sub>4</sub> furnished  
1,3-diarylimidazolidines, while their deprotonation with KH in THF gave  
access to stable carbenes, 1,3-diarylimidazolin-2-ylidenes. Similarly  
substituted imidazol-2-ylidenes are described for comparison.  
ST **glyoxal** aniline cyclocondensation; imidazolylidene prepn;  
imidazolinylidene prepn; imidazolidine prepn  
IT Carbenes (methylene derivatives)  
RL: PRP (Properties); RCT (Reactant); SPN (Synthetic preparation); PREP  
(Preparation); RACT (Reactant or reagent)  
(preparation and structure of imidazolylidenes and imidazolinylidenes)  
IT 258278-26-1P 258278-31-8P  
RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation)  
(crystal structure)  
IT 244187-81-3P  
RL: PRP (Properties); RCT (Reactant); SPN (Synthetic preparation); PREP  
(Preparation); RACT (Reactant or reagent)  
(crystal structure and chlorination)  
IT 250285-32-6P  
RL: PRP (Properties); RCT (Reactant); SPN (Synthetic preparation)  
; PREP (Preparation); RACT (Reactant or reagent)  
(crystal structure and reduction)  
IT 88-05-1, 2,4,6-Trimethylaniline 107-22-2, **Glyoxal**  
3188-13-4, Chloromethyl ethyl ether 24544-04-5, 2,6-Diisopropylaniline  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(preparation of imidazolylidenes, imidazolinylidenes, and imidazolidines)  
IT 56222-36-7P 74663-75-5P 141556-42-5P 141556-45-8P  
173035-10-4P 258278-23-8P 258278-24-9P 258278-25-0P  
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT  
(Reactant or reagent)  
(preparation of imidazolylidenes, imidazolinylidenes, and imidazolidines)  
IT 173035-11-5P 200730-48-9P 258278-27-2P 258278-28-3P  
RL: SPN (Synthetic preparation); PREP (Preparation)  
(preparation of imidazolylidenes, imidazolinylidenes, and imidazolidines)  
RE.CNT 35 THERE ARE 35 CITED REFERENCES AVAILABLE FOR THIS RECORD  
RE  
(1) Alder, R; Angew Chem, Int Ed Engl 1996, V35, P1121 HCAPLUS  
(2) Alder, R; Chem Commun (Cambridge) 1997, P1513 HCAPLUS  
(3) Alder, R; J Am Chem Soc 1998, V120, P11526 HCAPLUS  
(4) Arduengo, A; Angew Chem, Int Ed Engl 1998, V37, P1963 HCAPLUS  
(5) Arduengo, A; J Am Chem Soc 1992, V114, P5530 HCAPLUS  
(6) Arduengo, A; J Am Chem Soc 1994, V116, P6361 HCAPLUS  
(7) Arduengo, A; J Am Chem Soc 1995, V117, P11027 HCAPLUS  
(8) Arduengo, A; J Am Chem Soc 1995, V117, P572 HCAPLUS  
(9) Arduengo, A; J Am Chem Soc 1997, V119, P12742 HCAPLUS  
(10) Arduengo, A; Liebigs Ann 1997, P365 HCAPLUS  
(11) Arduengo, A; Organometallics 1998, V17, P3375 HCAPLUS  
(12) Arduengo, A; US 5077414 Preparation of 1,3-Disubstituted Imidazolium Salts  
1991 HCAPLUS  
(13) Arduengo, A; To be published in Acc Chem Res 1999, P32  
(14) Arduengo, A; unpublished results  
(15) Chen, H; Inorg Chem 1991, V30, P2487 HCAPLUS  
(16) Denk, M; Angew Chem, Int Ed Engl 1997, V36, P2607 HCAPLUS  
(17) Herrmann, W; Chem-Eur J 1996, V2, P772 HCAPLUS  
(18) Hocker, J; Chem Ber 1972, V105, P1651 HCAPLUS  
(19) Hocker, J; Justus Liebigs Ann Chem 1971, V751, P145 HCAPLUS  
(20) Huang, J; J Am Chem Soc 1999, V121, P2674 HCAPLUS  
(21) Huang, J; Organometallics 1999, V18, P2370 HCAPLUS  
(22) Jaenicke, L; Liebigs Ann Chem 1959, V624, P120 HCAPLUS



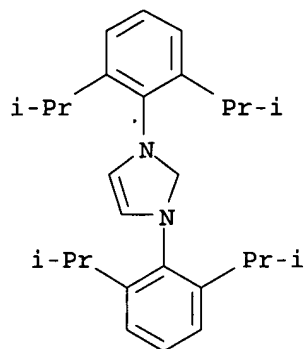
- (23) Jafarpour, L; Organometallics 1999, V18, P3760 HCAPLUS
- (24) Keller, E; SCHAKAL
- (25) Kuhn, N; Synthesis 1993, V1993, P561
- (26) Nishiyama, T; J Heterocycl Chem 1988, V25, P1773 HCAPLUS
- (27) Perrin, D; Purification of Laboratory Chemicals; 2nd ed 1985
- (28) Taton, T; Angew Chem, Int Ed Engl 1996, V35, P1011 HCAPLUS
- (29) Wanzlick, H; Angew Chem 1960, V72, P494 HCAPLUS
- (30) Wanzlick, H; Angew Chem 1962, V74, P128
- (31) Wanzlick, H; Chem Ber 1953, V86, P1463 HCAPLUS
- (32) Wanzlick, H; Chem Ber 1961, V74, P2389
- (33) Wanzlick, H; Chem Ber 1963, V96, P1208 HCAPLUS
- (34) Zettlitzer, M; Chem Ber 1986, V119, P1868 HCAPLUS
- (35) Zhang, C; J Org Chem 1999, V64, P3804 HCAPLUS

IT 250285-32-6P

RL: PRP (Properties); RCT (Reactant); SPN (Synthetic preparation)  
; PREP (Preparation); RACT (Reactant or reagent)  
(crystal structure and reduction).

RN 250285-32-6 HCAPLUS

CN 1H-Imidazolium, 1,3-bis[2,6-bis(1-methylethyl)phenyl]-, chloride (9CI)  
(CA INDEX NAME)



● Cl<sup>-</sup>

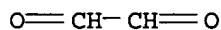
ONE OR MORE TAUTOMERIC DOUBLE BONDS NOT DISPLAYED IN THE STRUCTURE

IT 107-22-2, Glyoxal

RL: RCT (Reactant); RACT (Reactant or reagent)  
(preparation of imidazolyliidenes, imidazolinylidenes, and imidazolidines)

RN 107-22-2 HCAPLUS

CN Ethanedial (9CI) (CA INDEX NAME)

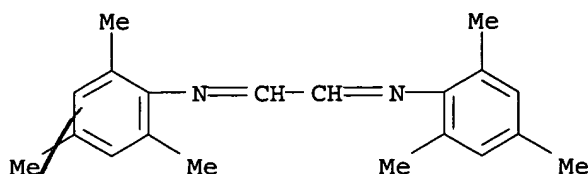


IT 56222-36-7P

RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT  
(Reactant or reagent)  
(preparation of imidazolyliidenes, imidazolinylidenes, and imidazolidines)

RN 56222-36-7 HCAPLUS

CN Benzenamine, N,N'-1,2-ethanediylidenebis[2,4,6-trimethyl- (9CI) (CA INDEX  
NAME)



L62 ANSWER 4 OF 4 HCAPLUS COPYRIGHT 2005 ACS on STN  
 AN 1999:643360 HCAPLUS  
 DN 132:49760  
 ED Entered STN: 11 Oct 1999  
 TI Efficient Cross-Coupling of Aryl Chlorides with Aryl Grignard Reagents  
 (Kumada Reaction) Mediated by a Palladium/Imidazolium Chloride System  
 AU Huang, Jinkun; Nolan, Steven P.  
 CS Department of Chemistry, University of New Orleans, New Orleans, LA,  
 70148, USA  
 SO Journal of the American Chemical Society (1999), 121(42),  
 9889-9890  
 CODEN: JACSAT; ISSN: 0002-7863  
 PB American Chemical Society  
 DT Journal  
 LA English  
 CC 25-1 (Benzene, Its Derivatives, and Condensed Benzenoid Compounds)  
 OS CASREACT 132:49760  
 AB A general methodol. for the Kumada reaction was presented. In the  
 presence of tris[μ-[(1,2-η:4,5-η)-(1E,4E)-1,5-diphenyl-1,4-  
 pentadien-3-one]]dipalladium or palladium diacetate and an imidazolium  
 chloride, aryl chlorides, aryl bromides or aryl iodides underwent a  
 coupling reaction to give biphenyl derivs. Suitable imidazolium compds.  
 were 1,3-bis(2,4,6-trimethylphenyl)-1H-imidazolium chloride and  
 1,3-bis[2,6-bis(1-methylethyl)phenyl]-1H-imidazolium chloride.  
 ST crosscoupling aryl chloride Grignard reagent Kumada; biphenyl  
 phenylnaphthalene prepn  
 IT Cross-coupling reaction  
 (Kumada reaction; cross-coupling of aryl chlorides with aryl Grignard  
 reagents (Kumada reaction) mediated by palladium and imidazolium  
 chloride)  
 IT Aryl halides  
 Aryl halides  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (aryl chlorides; cross-coupling of aryl chlorides with aryl Grignard  
 reagents (Kumada reaction) mediated by palladium and imidazolium  
 chloride)  
 IT Aryl halides  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (aryl iodides; cross-coupling of aryl chlorides with aryl Grignard  
 reagents (Kumada reaction) mediated by palladium and imidazolium  
 chloride)  
 IT Chlorides, reactions  
 Chlorides, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (aryl; cross-coupling of aryl chlorides with aryl Grignard reagents  
 (Kumada reaction) mediated by palladium and imidazolium chloride)  
 IT Cross-coupling reaction catalysts  
 (cross-coupling of aryl chlorides with aryl Grignard reagents (Kumada  
 reaction) mediated by palladium and imidazolium chloride)  
 IT Aryl bromides  
 Grignard reagents  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (cross-coupling of aryl chlorides with aryl Grignard reagents (Kumada

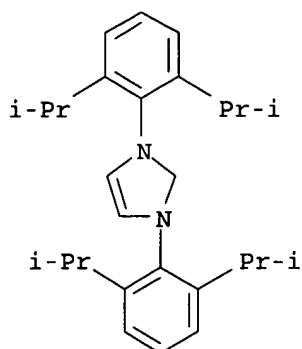
- reaction) mediated by palladium and imidazolium chloride)
- IT 3375-31-3, Palladium diacetate 51364-51-3, Tris[ $\mu$ -(1,2- $\eta$ :4,5- $\eta$ )-(1E,4E)-1,5-diphenyl-1,4-pentadien-3-one]]dipalladium  
141556-45-8, 1,3-Bis(2,4,6-trimethylphenyl)-1H-imidazolium chloride  
RL: CAT (Catalyst use); USES (Uses)  
(cross-coupling of aryl chlorides with aryl Grignard reagents mediated by palladium and imidazolium chloride)
- IT 250285-32-6P, 1,3-Bis[2,6-bis(1-methylethyl)phenyl]-1H-imidazolium chloride  
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP (Preparation); USES (Uses)  
(cross-coupling of aryl chlorides with aryl Grignard reagents mediated by palladium and imidazolium chloride)
- IT 95-72-7, 1-Chloro-2,5-dimethylbenzene 100-58-3, Phenylmagnesium bromide  
106-38-7, 1-Bromo-4-methylbenzene 106-43-4, 1-Chloro-4-methylbenzene  
106-48-9, 4-Chlorophenol 107-22-2, Glyoxal 446-53-7,  
(2-Fluorophenyl)magnesium bromide 540-38-5, 4-Iodophenol 619-42-1  
623-12-1, 1-Chloro-4-methoxybenzene 2633-66-1, (2,4,6-Trimethylphenyl)magnesium bromide 4294-57-9, (4-Methylphenyl)magnesium bromide 5111-65-9, 2-Bromo-6-methoxynaphthalene 6781-98-2,  
1-Chloro-2,6-dimethylbenzene 24544-04-5, 2,6-Diisopropylaniline 28987-79-3, (3-Methylphenyl)magnesium bromide  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(cross-coupling of aryl chlorides with aryl Grignard reagents mediated by palladium and imidazolium chloride)
- IT 74663-75-5P  
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)  
(cross-coupling of aryl chlorides with aryl Grignard reagents mediated by palladium and imidazolium chloride)
- IT 92-69-3P, [1,1'-Biphenyl]-4-ol 613-37-6P, 4-Methoxy-1,1'-biphenyl  
644-08-6P, 4-Methyl-1,1'-biphenyl 720-75-2P, [1,1'-Biphenyl]-4-carboxylic acid, methyl ester 3976-34-9P, 2,6-Dimethyl-1,1'-biphenyl  
7372-85-2P, 2,5-Dimethyl-1,1'-biphenyl 17171-17-4P 39502-90-4P,  
4'-Methoxy-2,4,6-trimethyl-1,1'-biphenyl 53040-92-9P,  
4-Methoxy-4'-methyl-1,1'-biphenyl 59115-43-4P, 2-Methoxy-6-phenylnaphthalene 72093-47-1P, 2-Fluoro-4'-methoxy-1,1'-biphenyl  
RL: SPN (Synthetic preparation); PREP (Preparation)  
(preparation of)

RE.CNT 64 THERE ARE 64 CITED REFERENCES AVAILABLE FOR THIS RECORD

RE

- (1) Anon; Chem Eng News July 13 71 1998
- (2) Anon; Chem Eng News June 1 1998
- (3) Anon; Homogeneous Catalysis with Metal Phosphine Complexes
- (4) Arduengo, A; Chem Ztg 1998, V32, P6 HCAPLUS
- (5) Arduengo, A; J Am Chem Soc 1992, V116, P4391
- (6) Arduengo, A; J Am Chem Soc 1992, V114, P5530 HCAPLUS
- (7) Barba, I; Tetrahedron 1990, V46, P7813 HCAPLUS
- (8) Bei, X; Tetrahedron Lett 1999, V40, P1237 HCAPLUS
- (9) Bei, X; Tetrahedron Lett 1999, V40, P3855 HCAPLUS
- (10) Bell, H; Aust J Chem 1979, V32, P1531 HCAPLUS
- (11) Bourelle-Warhnier, F; J Org Chem 1980, V45, P428
- (12) Busacca, C; Tetrahedron Lett 1999, V40, P3101 HCAPLUS
- (13) Collman, J; Principles and Applications of Organotransition Metal Chemistry 1987
- (14) Cornils, B; Applied Homogeneous Catalysis with Organometallic Compounds 1996
- (15) Corriu, R; Chem Soc, Chem Commun 1972, P144 HCAPLUS
- (16) Farina, V; J Org Chem 1993, V58, P5434 HCAPLUS
- (17) Hamann, B; J Am Chem Soc 1998, V120, P7369 HCAPLUS
- (18) Hayashi, T; J Am Chem Soc 1982, V104, P180 HCAPLUS
- (19) Hayashi, T; J Am Chem Soc 1984, V106, P158 HCAPLUS
- (20) Heck, R; Palladium Reagents in Organic Syntheses 1985

- (21) Herrmann, W; Angew Chem, Int Ed Engl 1995, V34, P2371 HCAPLUS  
(22) Herrmann, W; Angew Chem, Int Ed Engl 1996, V35, P2805 HCAPLUS  
(23) Herrmann, W; Angew Chem, Int Ed Engl 1997, V36, P2163  
(24) Herrmann, W; Chem Eur J 1996, V2, P772 HCAPLUS  
(25) Herrmann, W; J Organomet Chem 1998, V557, P93 HCAPLUS  
(26) Huang, J; J Am Chem Soc 1999, V121, P2674 HCAPLUS  
(27) Huang, J; Manuscript submitted for publication  
(28) Huang, J; Organometallics 1999, V18, P2370 HCAPLUS  
(29) Indolese, A; Tetrahedron Lett 1997, V38, P3513 HCAPLUS  
(30) Jendralla, H; Synthesis 1990, P827 HCAPLUS  
(31) Kamikawa, T; Synlett 1997, P163 HCAPLUS  
(32) Kang, S; J Org Chem 1996, V61, P4720 HCAPLUS  
(33) Kumada, M; Pure Appl Chem 1980, V52, P669 HCAPLUS  
(34) Littke, A; Int Ed Engl 1998, V37, P3387 HCAPLUS  
(35) Littke, A; J Org Chem 1999, V64, P10 HCAPLUS  
(36) Lourak, M; J Org Chem 1989, V54, P4844 HCAPLUS  
(37) McGuinness, D; J Organomet Chem 1998, V165, P16  
(38) Miller, J; Tetrahedron Lett 1998, V39, P7275 HCAPLUS  
(39) Minato, A; Tetrahedron Lett 1981, V22, P5319 HCAPLUS  
(40) Miyaura, N; Chem Rev 1995, V95, P2457 HCAPLUS  
(41) Old, D; J Am Chem Soc 1998, V120, P9722 HCAPLUS  
(42) Parshall, G; Homogeneous Catalysis 1992  
(43) Rao, M; Synthesis 1987, P231  
(44) Reetz, M; Angew Chem Int Ed Engl 1998, V37, P481 HCAPLUS  
(45) Regitz, M; Angew Chem, Int Ed Engl 1996, V35, P725 HCAPLUS  
(46) Saito, S; J Org Chem 1997, V62, P8024 HCAPLUS  
(47) Saito, S; Tetrahedron Lett 1996, V37, P2993 HCAPLUS  
(48) Schoervarrs, A; J Org Chem 1997, V62, P4943  
(49) Scholl, M; Tetrahedron Lett 1999, V40, P2247 HCAPLUS  
(50) Sekiya, A; J Organomet 1976, V118, P349 HCAPLUS  
(51) Shishido, K; J Chem Soc Perkin Trans 1990, V1, P469  
(52) Sofia, A; J Org Chem 1999, V64, P1745  
(53) Stanforth, S; Tetrahedron 1998, V54, P263 HCAPLUS  
(54) Tamao, K; Bull Chem Soc Jpn 1976, V49, P1958 HCAPLUS  
(55) Tamao, K; J Am Chem Soc 1972, V94, P4374 HCAPLUS  
(56) Tamao, K; J Am Chem Soc 1972, V94, P9268 HCAPLUS  
(57) Trost, B; Comprehensive Organometallic Chemistry 1982, V8, P799  
(58) Tsuji, J; Palladium Reagents and Catalysts 1995  
(59) Tsuji, J; Synthesis 1990, P739 HCAPLUS  
(60) Voges, M; Organometallics 1999, V18, P529 HCAPLUS  
(61) Weskamp, T; Angew Chem, Int Ed Engl 1998, V37, P2490 HCAPLUS  
(62) Widdowson, D; Tetrahedron 1986, V42, P2111 HCAPLUS  
(63) Yamamura, M; J Organomet Chem 1975, V91, P339 HCAPLUS  
(64) Zhang, C; J Org Chem, in press 1999
- IT 250285-32-6P, 1,3-Bis[2,6-bis(1-methylethyl)phenyl]-1H-imidazolium  
chloride  
RL: CAT (Catalyst use); SPN (Synthetic preparation); PREP  
(Preparation); USES (Uses)  
(cross-coupling of aryl chlorides with aryl Grignard reagents mediated  
by palladium and imidazolium chloride)
- RN 250285-32-6 HCAPLUS  
CN 1H-Imidazolium, 1,3-bis[2,6-bis(1-methylethyl)phenyl]-, chloride (9CI)  
(CA INDEX NAME)



● Cl<sup>-</sup>

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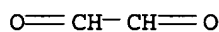
IT 107-22-2, Glyoxal

RL: RCT (Reactant); RACT (Reactant or reagent)

(cross-coupling of aryl chlorides with aryl Grignard reagents mediated by palladium and imidazolium chloride)

RN 107-22-2 HCAPLUS

CN Ethanedial (9CI) (CA INDEX NAME)



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FILE CONTENT:1840 - 20 Mar 2005 VOL 142 ISS 12

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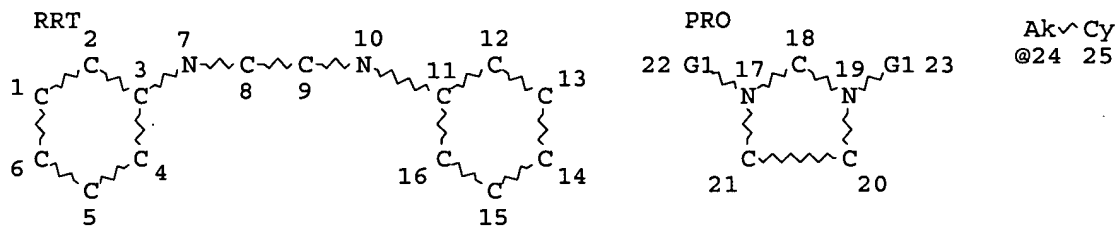
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This file contains CAS Registry Numbers for easy and accurate substance identification.

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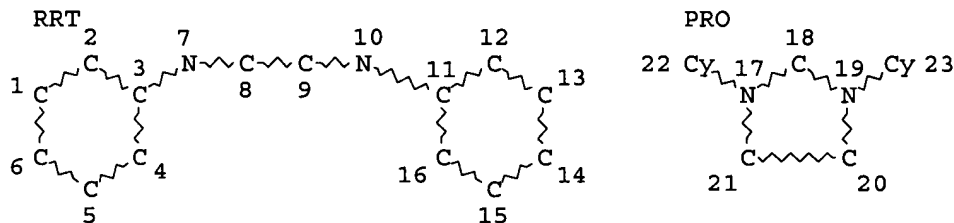
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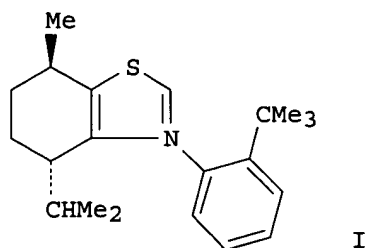
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 L75 6 SEA FILE=CASREACT ABB=ON PLU=ON L74 AND (IMIDAZOL? OR  
 DIARYLIMID?)/TI  
 L76 4 SEA FILE=CASREACT ABB=ON PLU=ON L75 NOT (OXALA? OR OXALIC?)/T  
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 L77 4 SEA FILE=CASREACT ABB=ON PLU=ON L76 AND (L70 OR L71 OR L74)

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L77 ANSWER 1 OF 4 CASREACT COPYRIGHT 2005 ACS on STN  
 AN 141:140358 CASREACT  
 TI Preparation of axially chiral N,N'-diarylimidazolium and

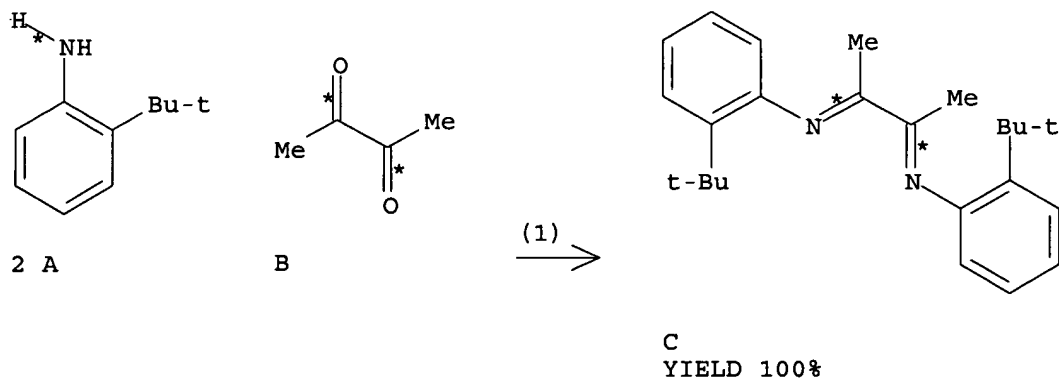
N-arylthiazolium salts and evaluation of their catalytic potential in the benzoin and in the intramolecular Stetter reactions

AU Pesch, Jens; Harms, Klaus; Bach, Thorsten  
 CS Lehrstuhl fuer Organische Chemie I, Technische Universitaet Muenchen, Garching, 85747, Germany  
 SO European Journal of Organic Chemistry (2004), (9), 2025-2035  
 CODEN: EJOCFK; ISSN: 1434-193X  
 PB Wiley-VCH Verlag GmbH & Co. KGaA  
 DT Journal  
 LA English  
 GI



AB N-Aryl-substituted imidazoles were prepared which contain a stereogenic axis and which can occur as atropisomers. The di(2-isopropylphenyl)imidazolium salts could be obtained from 2-isopropylaniline and diacetyl in three steps (19% yield) whereas the synthesis of their tert-Bu analogs failed. The meso-isomer prevailed (dr = 90/10). Chiral thiazolium salts were prepared in two steps from 2-tert-butylaniline. The enantiomerically pure thiazolium salt I was obtained from  $\alpha$ -bromomenthone and 2-tert-butylaniline (27% overall yield). In contrast to the imidazolium salts, the thiazolium salts proved to be suitable catalysts in the benzoin condensation of benzaldehyde and in the intramol. Stetter reaction of 2-OCHC6H4OCH2CH:CHCO2Me. The best results obtained with catalyst I (20 mol %) were 85% (R)-PhCOCHPhOH (40% ee) and 75% Me (R)-4-oxochroman-3-acetate. The stereogenic axis of I is not configurationally stable in the catalytically active carbene intermediate. The catalyst is recovered as a mixture of diastereomeric atropisomers in a ratio of 70:30 to 75:25.

RX(1) OF 30 2 A + B ==> C



RX(1) RCT A 6310-21-0, B 431-03-8

PRO C 181707-42-6  
 CAT 64-18-6 HCO2H  
 SOL 64-17-5 EtOH

## RETABLE

Referenced Author (RAU)	Year (RPY)	VOL (RVL)	PG (RPG)	Referenced Work (RWK)	Referenced File
Arduengo, A	1999	32	913	Acc Chem Res	CAPLUS
Arduengo, A	1998	110	2062	Angew Chem	
Arduengo, A	1998	37	1963	Angew Chem Int Ed	CAPLUS
Bach, T	1999	40	9003	Tetrahedron Lett	CAPLUS
Bourissou, D	2000	100	39	Chem Rev	CAPLUS
Breslow, R	1958	80	3719	J Am Chem Soc	CAPLUS
Breslow, R	1959	81	3080	J Am Chem Soc	CAPLUS
Breslow, R	1996	37	8241	Tetrahedron Lett	CAPLUS
CCDC				www.ccdc.cam.ac.uk/c	
CCDC				www.ccdc.cam.ac.uk/c	
CCDC				www.ccdc.cam.ac.uk/c	
CCDC				www.ccdc.cam.ac.uk/c	
CCDC				www.ccdc.cam.ac.uk/c	
Ciganek, E	1995		1311	Synthesis	CAPLUS
Djafri, A	1985		273	J Chem Soc, Perkin T	CAPLUS
Djafri, A	1996	6	123	J Soc, Alger Chim	CAPLUS
Dvorak, C	1998	39	2925	Tetrahedron Lett	CAPLUS
Enders, D	2002	114	1822	Angew Chem	
Enders, D	2002	41	1743	Angew Chem Int Ed	CAPLUS
Enders, D	1999	3	1093	Comprehensive Asymme	CAPLUS
Enders, D	1996	79	1217	Helv Chim Acta	CAPLUS
Enders, D	1996	79	1899	Helv Chim Acta	CAPLUS
Enders, D	2003		1292	Synthesis	CAPLUS
Gallo, R	1988	43	173	Adv Heterocycl Chem	CAPLUS
Gerhard, A	1997	38	3615	Tetrahedron Lett	CAPLUS
Hassner, A	1991	1	541	Comprehensive Organi	
Herrmann, W	1997	109	2256	Angew Chem	
Herrmann, W	2002	114	1342	Angew Chem	
Herrmann, W	2002	41	1290	Angew Chem Int Ed	CAPLUS
Herrmann, W	1997	36	2162	Angew Chem Int Ed En	CAPLUS
Hirtopceanu, A	2000		1081	Eur J Org Chem	CAPLUS
Hirtopceanu, A	2000	53	1669	Heterocycles	CAPLUS
Ide, W	1948	4	269	Org React	CAPLUS
Kerr, M	2002	124	10298	J Am Chem Soc	CAPLUS
Kerr, M	2003		1934	Synlett	CAPLUS
Knight, R	1997	38	3611	Tetrahedron Lett	CAPLUS
Leeper, F	1995		861	J Chem Soc, Perkin T	CAPLUS
Leeper, F	1998		1891	J Chem Soc, Perkin T	
Liebscher, J	1994	E8b	192	Houben-Weyl, 4th ed	
Marti, J	1993	34	521	Tetrahedron Lett	CAPLUS
Pesch, J	2000			Diploma Thesis, Univ	
Peters, K	1998	213	503	Z Kristallogr	CAPLUS
Pohl, M	2002	8	5288	Chem Eur J	CAPLUS
Regitz, M	1996	108	791	Angew Chem	
Regitz, M	1997	35	724	Angew Chem Int Ed En	
Roussel, C	1997	761	129	J Chromatogr A	CAPLUS
Roussel, C	1988	53	5076	J Org Chem	CAPLUS
Roussel, C	1988	12	947	New J Chem	CAPLUS
Schonherr, H	1970	731	176	Justus Liebigs Ann C	
Seiders, T	2001	3	3225	Org Lett	CAPLUS
Sheehan, J	1966	88	3666	J Am Chem Soc	CAPLUS
Sheehan, J	1974	39	1196	J Org Chem	CAPLUS
Stetter, H	1973	85	89	Angew Chem	CAPLUS
Stetter, H	1974	86	589	Angew Chem	CAPLUS
Stetter, H	1976	88	695	Angew Chem	CAPLUS
Stetter, H	1973	12	81	Angew Chem Int Ed En	



Stetter, H	1974	13	539	Angew Chem Int Ed En	
Stetter, H	1976	15	639	Angew Chem Int Ed En	
Stetter, H	1991	40	407	Org React	CAPLUS
Still, W	1978	43	2923	J Org Chem	CAPLUS
Tagaki, W	1980	53	478	Bull Chem Soc Jpn	CAPLUS
Teles, J	1996	79	61	Helv Chim Acta	CAPLUS
Tempel, D	2000	122	6686	J Am Chem Soc	CAPLUS
Ukai, T	1943	63	112	J Pharm Soc, Jpn	
Uscumlic, G	1994		1799	J Chem Soc, Perkin T	CAPLUS
Wohler, F	1832	3	249	Ann Pharm	
Wolf, C	1995		781	Liebigs Ann	CAPLUS
Zhao, C	1988	46	784	Huaxue Xuebao	CAPLUS

L77 ANSWER 2 OF 4 CASREACT COPYRIGHT 2005 ACS on STN

AN 133:362823 CASREACT

TI A sterically demanding nucleophilic carbene: 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene. Thermochemistry and catalytic application in olefin metathesis

AU Jafarpour, L.; Stevens, E. D.; Nolan, S. P.

CS Department of Chemistry, University of New Orleans, New Orleans, LA, 70148, USA

SO Journal of Organometallic Chemistry (2000), 606(1), 49-54  
CODEN: JORCAI; ISSN: 0022-328X

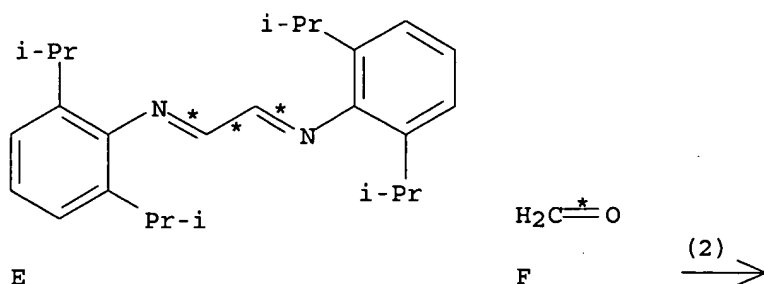
PB Elsevier Science S.A.

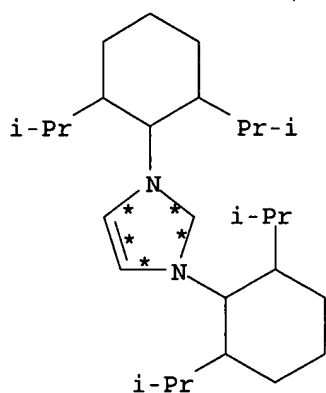
DT Journal

LA English

AB The sterically demanding nucleophilic carbene ligand 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr, 4) has been synthesized. The reaction of [Cp\*RuCl]<sub>4</sub> (5; Cp\* = η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>) with this ligand affords a coordinatively unsatd. Cp\*Ru(IPr)Cl (6) complex. Solution calorimetric results in this system provide information concerning the electron donor properties of the carbene ligand. Steric parameters associated with this ligand are determined from the x-ray crystal structure study. The carbene ligand reacts with RuCl<sub>2</sub>(C(H)Ph)(PCy<sub>3</sub>)<sub>2</sub> to yield a mixed carbene-phosphine ruthenium complex RuCl<sub>2</sub>(C(H)Ph)(IPr)(PCy<sub>3</sub>) (9). A single-crystal x-ray diffraction study has been performed on 9. The thermal stability of 9 has been studied at 60° and its catalytic activity has been evaluated for the ring closing metathesis of di-Et diallylmalonate.

RX(2) OF 15 ...E + F ==> G...





● Cl<sup>-</sup>

G  
YIELD 47%

RX(2) RCT E 74663-75-5, F 50-00-0

STAGE(1)

SOL 108-88-3 PhMe

STAGE(2)

RGT H 7647-01-0 HCl

SOL 123-91-1 Dioxane

PRO G 250285-32-6

NTE PARAFORMALDEHYDE USED

RETABLE

Referenced Author (RAU)	Year (RPY)	VOL (RVL)	PG (RPG)	Referenced Work (RWK)	Referenced File
Ackermann, L	1999	40	4787	Tetrahedron Lett	CAPLUS
Anon				private communicatio	
Arduengo, A	1991			US 5077414	CAPLUS
Arduengo, A	1998	32	6	Chem Z	CAPLUS
Arduengo, A	1992	114	5530	J Am Chem Soc	CAPLUS
Campion, B	1998		278	J Chem Soc Chem Comm	
Collman, J	1987			Principles and Appli	
Demonceau, A	1997	30	3127	Macromolecules	CAPLUS
Diaz, E	1997	119	3887	J Am Chem Soc	
Fagan, P	1998	110	2981	J Am Chem Soc	
Herrmann, W	1996	35	1087	Angew Chem Int Ed En	CAPLUS
Huang, J	1999	121	2674	J Am Chem Soc	CAPLUS
Huang, J	1999	18	2370	Organometallics	CAPLUS
Kilday, M	1980	85	467	Res Natl Bur Stand (	CAPLUS
Kingsbury, J	1999	121	791	J Am Chem Soc	CAPLUS
Lappert, M	1988	358	185	J Organomet Chem	CAPLUS
Luo, L	1994	13	4781	Organometallics	CAPLUS
Mohr, B	1996	15	4317	Organometallics	CAPLUS
Nguyen, S	1992	114	3974	J Am Chem Soc	CAPLUS
Nguyen, S	1993	115	9858	J Am Chem Soc	CAPLUS
Nolan, S	1986	25	4446	Inorg Chem	CAPLUS
Nolan, S	1985	282	357	J Organomet Chem	CAPLUS
Ojelund, G	1968	22	1691	Acta Chem Scand	
Parshall, G	1992			Homogeneous Catalysi	

Perrin, D	1988			Purification of Labo	
Pignolet, L	1983			Homogeneous Catalysi	
Scholl, M	1999	40	2247	Tetrahedron Lett	CAPLUS
Schwab, P	1995	34	2039	Angew Chem Int Ed En	CAPLUS
Schwab, P	1996	118	100	J Am Chem Soc	CAPLUS
Serron, S	1998	13	534	Organometallics	
Stumpf, A	1995		1127	J Chem Soc Chem Comm	
Ulman, M	1998	17	2484	Organometallics	CAPLUS
Wanzlick, H	1962	1	75	Angew Chem Int Ed En	
Wu, Z	1995	117	5503	J Am Chem Soc	CAPLUS
Yang, K	1997	16	5234	Organometallics	CAPLUS

L77 ANSWER 3 OF 4 CASREACT COPYRIGHT 2005 ACS on STN

AN 132:151738 CASREACT

TI **Imidazolylidenes, imidazolinyliidenes and imidazolidines**

AU Arduengo, Anthony J., III; Krafczyk, Roland; Schmutzler, Reinhard; Craig, Hugh A.; Goerlich, Jens R.; Marshall, William J.; Unverzagt, Markus

CS Institut fur Anorganische und Analytische Chemie, der Technischen Universitat - Carolo Wilhelmina, Braunschweig, D-38106, Germany

SO Tetrahedron (1999), 55(51), 14523-14534

CODEN: TETRAB; ISSN: 0040-4020

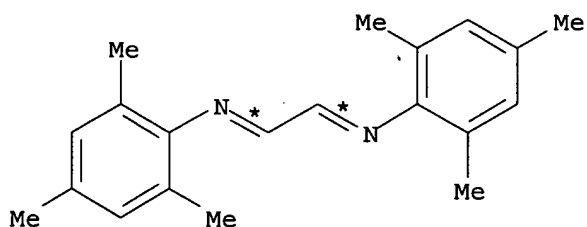
PB Elsevier Science Ltd.

DT Journal

LA English

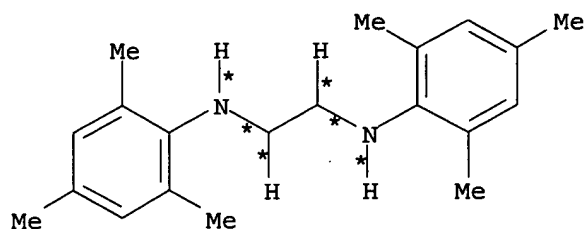
AB Starting from glyoxal and RNH<sub>2</sub> [R = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>, 2,6-(Me<sub>2</sub>CH)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>], the corresponding 1,3-diarylimidazolium chlorides were obtained in a 3-step sequence via diimines and ethylenediamine dihydrochlorides. Subsequent reduction with LiAlH<sub>4</sub> furnished 1,3-diarylimidazolidines, while their deprotonation with KH in THF gave access to stable carbenes, 1,3-diarylimidazol-2-ylidenes. Similarly substituted imidazol-2-ylidenes are described for comparison.

RX(1) OF 14 A ==> B



A





● 2 HCl

B  
YIELD 85%

RX(1) RCT A 56222-36-7

STAGE(1)

RGT C 16940-66-2 NaBH<sub>4</sub>

SOL 109-99-9 THF

STAGE(2)

RGT D 7647-01-0 HCl

SOL 7732-18-5 Water, 76-05-1 F3CCO<sub>2</sub>H

PRO B 258278-23-8

RETABLE

Referenced Author (RAU)	Year (RPY)	VOL (RVL)	PG (RPG)	Referenced Work (RWK)	Referenced File
=====	=====	=====	=====	=====	=====
Alder, R	1996	35	1121	Angew Chem, Int Ed E	CAPLUS
Alder, R	1997		1513	Chem Commun (Cambrid	CAPLUS
Alder, R	1998	120	11526	J Am Chem Soc	CAPLUS
Arduengo, A	1998	37	1963	Angew Chem, Int Ed E	CAPLUS
Arduengo, A	1992	114	5530	J Am Chem Soc	CAPLUS
Arduengo, A	1994	116	6361	J Am Chem Soc	CAPLUS
Arduengo, A	1995	117	11027	J Am Chem Soc	CAPLUS
Arduengo, A	1995	117	572	J Am Chem Soc	CAPLUS
Arduengo, A	1997	119	12742	J Am Chem Soc	CAPLUS
Arduengo, A	1997		365	Liebigs Ann	CAPLUS
Arduengo, A	1998	17	3375	Organometal	CAPLUS
Arduengo, A	1991			US 5077414	CAPLUS
Arduengo, A	1999		32	To be published in A	
Arduengo, A				unpublished results	
Chen, H	1991	30	2487	Inorg Chem	CAPLUS
Denk, M	1997	36	2607	Angew Chem, Int Ed E	CAPLUS
Herrmann, W	1996	2	772	Chem-Eur J	CAPLUS
Hocker, J	1972	105	1651	Chem Ber	CAPLUS
Hocker, J	1971	751	145	Justus Liebigs Ann C	CAPLUS
Huang, J	1999	121	2674	J Am Chem Soc	CAPLUS
Huang, J	1999	18	2370	Organometallics	CAPLUS
Jaenicke, L	1959	624	120	Liebigs Ann Chem	CAPLUS
Jafarpour, L	1999	18	3760	Organometallics	CAPLUS
Keller, E				SCHAKAL	
Kuhn, N	1993	1993	561	Synthesis	
Nishiyama, T	1988	25	1773	J Heterocycl Chem	CAPLUS
Perrin, D	1985			Purification of Labo	
Taton, T	1996	35	1011	Angew Chem, Int Ed E	CAPLUS
Wanzlick, H	1960	72	494	Angew Chem	CAPLUS
Wanzlick, H	1962	74	128	Angew Chem	

Wanzlick, H	1953	86	1463	Chem Ber	CAPLUS
Wanzlick, H	1961	74	2389	Chem Ber	
Wanzlick, H	1963	96	1208	Chem Ber	CAPLUS
Zettlitz, M	1986	119	1868	Chem Ber	CAPLUS
Zhang, C	1999	64	3804	J Org Chem	CAPLUS

L77 ANSWER 4 OF 4 CASREACT COPYRIGHT 2005 ACS on STN

AN 132:49760 CASREACT

TI Efficient Cross-Coupling of Aryl Chlorides with Aryl Grignard Reagents  
(Kumada Reaction) Mediated by a Palladium/Imidazolium Chloride  
System

AU Huang, Jinkun; Nolan, Steven P.

CS Department of Chemistry, University of New Orleans, New Orleans, LA,  
70148, USA

SO Journal of the American Chemical Society (1999), 121(42), 9889-9890  
CODEN: JACSAT; ISSN: 0002-7863

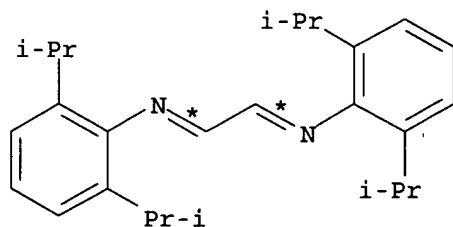
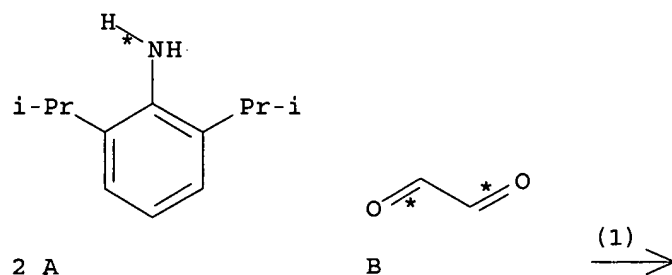
PB American Chemical Society

DT Journal

LA English

AB A general methodol. for the Kumada reaction was presented. In the  
presence of tris[μ-[(1,2-η:4,5-η)-(1E,4E)-1,5-diphenyl-1,4-  
pentadien-3-one]]dipalladium or palladium diacetate and an imidazolium  
chloride, aryl chlorides, aryl bromides or aryl iodides underwent a  
coupling reaction to give biphenyl derivs. Suitable imidazolium compds.  
were 1,3-bis(2,4,6-trimethylphenyl)-1H-imidazolium chloride and  
1,3-bis[2,6-bis(1-methylethyl)phenyl]-1H-imidazolium chloride.

RX(1) OF 16 2 A + B ==> C...



C  
YIELD 78%

RX(1) RCT A 24544-04-5, B 107-22-2  
PRO C 74663-75-5  
CAT 64-18-6 HCO2H

## SOL 7732-18-5 Water, 64-17-5 EtOH

## RETABLE

Referenced Author (RAU)	Year (RPY)	VOL (RVL)	PG (RPG)	Referenced Work (RWK)	Referenced File
=====	=====	=====	=====	=====	=====
Anon	1998			Chem Eng News July 1	
Anon	1998			Chem Eng News June 1	
Anon				Homogeneous Catalysi	
Arduengo, A	1998	32	6	Chem Ztg	CAPLUS
Arduengo, A	1992	116	4391	J Am Chem Soc	
Arduengo, A	1992	114	5530	J Am Chem Soc	CAPLUS
Barba, I	1990	46	7813	Tetrahedron	CAPLUS
Bei, X	1999	40	1237	Tetrahedron Lett	CAPLUS
Bei, X	1999	40	3855	Tetrahedron Lett	CAPLUS
Bell, H	1979	32	1531	Aust J Chem	CAPLUS
Bourelle-Warhnier, F	1980	45	428	J Org Chem	
Busacca, C	1999	40	3101	Tetrahedron Lett	CAPLUS
Collman, J	1987			Principles and Appli	
Cornils, B	1996			Applied Homogeneous	
Corriu, R	1972		144	Chem Soc, Chem Commu	CAPLUS
Farina, V	1993	58	5434	J Org Chem	CAPLUS
Hamann, B	1998	120	7369	J Am Chem Soc	CAPLUS
Hayashi, T	1982	104	180	J Am Chem Soc	CAPLUS
Hayashi, T	1984	106	158	J Am Chem Soc	CAPLUS
Heck, R	1985			Palladium Reagents i	
Herrmann, W	1995	34	2371	Angew Chem, Int Ed E	CAPLUS
Herrmann, W	1996	35	2805	Angew Chem, Int Ed E	CAPLUS
Herrmann, W	1997	36	2163	Angew Chem, Int Ed E	
Herrmann, W	1996	2	772	Chem Eur J	CAPLUS
Herrmann, W	1998	557	93	J Organomet Chem	CAPLUS
Huang, J	1999	121	2674	J Am Chem Soc	CAPLUS
Huang, J				Manuscript submitted	
Huang, J	1999	18	2370	Organometallics	CAPLUS
Indolese, A	1997	38	3513	Tetrahedron Lett	CAPLUS
Jendralla, H	1990		827	Synthesis	CAPLUS
Kamikawa, T	1997		163	Synlett	CAPLUS
Kang, S	1996	61	4720	J Org Chem	CAPLUS
Kumada, M	1980	52	669	Pure Appl Chem	CAPLUS
Littke, A	1998	37	3387	Int Ed Engl	CAPLUS
Littke, A	1999	64	10	J Org Chem	CAPLUS
Lourak, M	1989	54	4844	J Org Chem	CAPLUS
McGuinness, D	1998	165	16	J Organomet Chem	
Miller, J	1998	39	7275	Tetrahedron Lett	CAPLUS
Minato, A	1981	22	5319	Tetrahedron Lett	CAPLUS
Miyaura, N	1995	95	2457	Chem Rev	CAPLUS
Old, D	1998	120	9722	J Am Chem Soc	CAPLUS
Parshall, G	1992			Homogeneous Catalysi	
Rao, M	1987		231	Synthesis	
Reetz, M	1998	37	481	Angew Chem Int Ed En	CAPLUS
Regitz, M	1996	35	725	Angew Chem, Int Ed E	CAPLUS
Saito, S	1997	62	8024	J Org Chem	CAPLUS
Saito, S	1996	37	2993	Tetrahedron Lett	CAPLUS
Schoervarrs, A	1997	62	4943	J Org Chem	
Scholl, M	1999	40	2247	Tetrahedron Lett	CAPLUS
Sekiya, A	1976	118	349	J Organomet	CAPLUS
Shishido, K	1990	1	469	J Chem Soc Perkin Tr	
Sofia, A	1999	64	1745	J Org Chem	
Stanforth, S	1998	54	263	Tetrahedron	CAPLUS
Tamao, K	1976	49	1958	Bull Chem Soc Jpn	CAPLUS
Tamao, K	1972	94	4374	J Am Chem Soc	CAPLUS
Tamao, K	1972	94	9268	J Am Chem Soc	CAPLUS
Trost, B	1982	8	799	Comprehensive Organo	
Tsuji, J	1995			Palladium Reagents a	

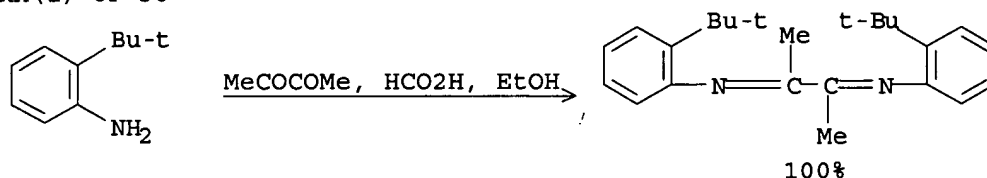
Tsuji, J	1990		739	Synthesis	CAPLUS
Voges, M	1999	18	529	Organometallics	CAPLUS
Weskamp, T	1998	37	2490	Angew Chem, Int Ed E	CAPLUS
Widdowson, D	1986	42	2111	Tetrahedron	CAPLUS
Yamamura, M	1975	91	C39	J Organomet Chem	CAPLUS
Zhang, C	1999			J Org Chem, in press	

=> d scan

L77 4 ANSWERS CASREACT COPYRIGHT 2005 ACS on STN

TI Preparation of axially chiral N,N'-diarylimidazolium and N-arylthiazolium salts and evaluation of their catalytic potential in the benzoin and in the intramolecular Stetter reactions

RX (1) OF 30

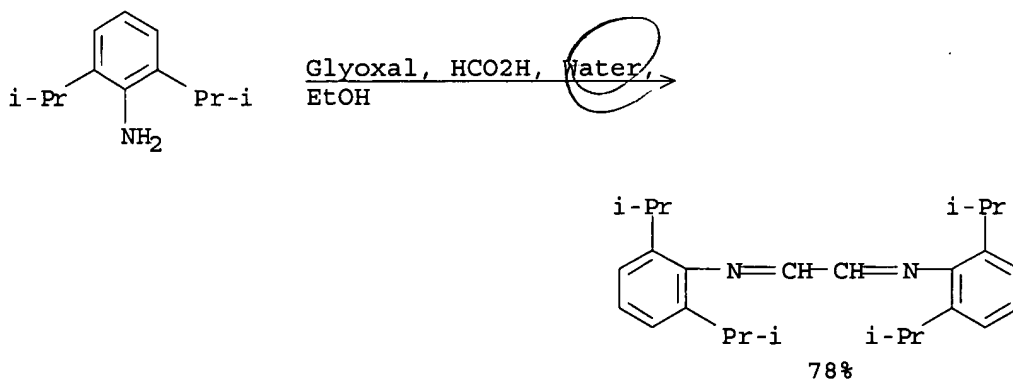


HOW MANY MORE ANSWERS DO YOU WISH TO SCAN? (1):

L77/4 ANSWERS CASREACT COPYRIGHT 2005 ACS on STN

Efficient Cross-Coupling of Aryl Chlorides with Aryl Grignard Reagents  
(Kumada Reaction) Mediated by a Palladium/**Imidazolium** Chloride  
System

RX (1) OF 16



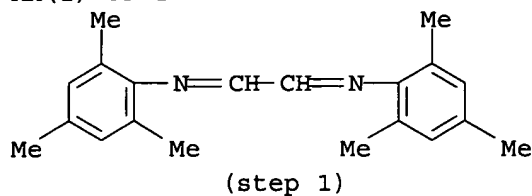
HOW MANY MORE ANSWERS DO YOU WISH TO SCAN? (1):

L77 4 ANSWERS CASREACT COPYRIGHT 2005 ACS on STN

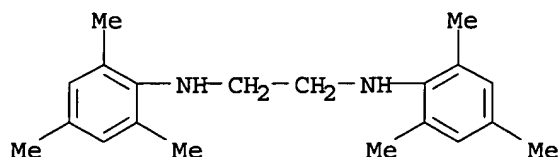
TI Imidazolyliidenes, imidazolinylidenes and  
imidazolidines

Tetrahedron

RX(1) OF 14



1. NaBH<sub>4</sub>, THF  
 2. HCl, Water,  
 F3CCO<sub>2</sub>H



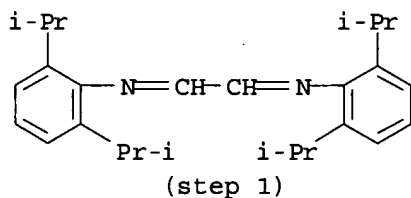
2 HCl  
 85%

HOW MANY MORE ANSWERS DO YOU WISH TO SCAN? (1):

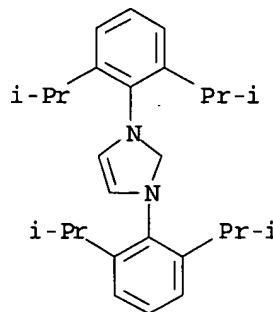
197 4 ANSWERS CASREACT COPYRIGHT 2005 ACS on STN

TI A sterically demanding nucleophilic carbene: 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene. Thermochemistry and catalytic application in olefin metathesis

RX(2) OF 15



1. HCHO, PhMe  
 2. HCl, Dioxane



Cl-  
 47%

NOTE: PARAFORMALDEHYDE USED

ALL ANSWERS HAVE BEEN SCANNED

=>

IS NOT A RECOGNIZED COMMAND

The previous command name entered was not recognized by the system. For a list of commands available to you in the current file, enter "HELP COMMANDS" at an arrow prompt (=>).



=> d his

(FILE 'HCAPLUS' ENTERED AT 14:12:00 ON 24 MAR 2005)

DEL HIS  
E NOLAN S/AU  
L1 75 S E3,E8,E30,E32,E35,E37  
L2 5 S L1 AND ?IMIDAZOL?  
L3 1 S L2 AND 1 3 DISUBSTITUTED  
L4 11 S 1 3 BIS 2 6 DIISOPROPYLPHENYL IMIDAZOLIUM CHLORIDE  
L5 14 S 1 3 BIS 2 6 DIISOPROPYLPHENYL IMIDAZOLIUM?  
L6 2 S L2 AND ?DIISOPROPYL?  
L7 3 S L2 AND (1 3 OR 2 6)  
L8 1 S L3 AND L6,L7  
L9 3 S L6-L8  
L10 2 S L9 AND BIS  
SEL RN

FILE 'REGISTRY' ENTERED AT 15:01:24 ON 24 MAR 2005

L11 11 S E1-E11  
L12 1 S L11 AND NCNC2/ES AND CL  
L13 1 S 286014-24-2  
L14 10 S 286014-24-2/CRN  
L15 1 S L14 AND I  
L16 2 S L12,L15  
L17 1 S L11 AND C2H2O2  
L18 1 S L11 AND C12H19N  
L19 1 S L11 AND C26H36N2  
E PARAFORMALDEHYDE/CN  
L20 1 S E3  
E HYDROCHLORIC ACID/CN  
L21 1 S E3  
E BF4H/MF  
L22 1 S 14874-70-5  
E TETRAFLUOROBOR/CN  
E F6P/MF  
L23 3 S E3  
L24 7 S L11 NOT CCS/CI

FILE 'HCAPLUS' ENTERED AT 15:31:22 ON 24 MAR 2005

L25 695 S ?DIAZABUTADIEN?  
L26 0 S L1 AND L25

FILE 'REGISTRY' ENTERED AT 15:32:31 ON 24 MAR 2005

L27 5 S (METHANOL OR ETHYL ACETATE OR ETHANOL OR TETRAHYDROFURAN OR T  
E C20H24N2/MF  
L28 153 S E3 AND 46.150.18/RID AND 2/NR  
L29 3 S L28 AND BENZENAMINE AND ETHANEDIYLIDENEBIS  
L30 2 S L29 AND TRIMETHYL  
L31 1 S DIOXANE/CN  
L32 1554 S 123-91-1/CRN  
L33 5 S L32 AND CLH  
L34 2 S L33 AND 2/NC  
L35 3 S L11 AND NCNC2/ES NOT L12,L13  
L36 1 S L35 AND C27H36N2  
L37 1 S 244187-81-3/CRN  
L38 1 S METHANOL/CN  
L39 1 S ETHYL ACETATE/CN

FILE 'HCAPLUS' ENTERED AT 15:37:56 ON 24 MAR 2005

L40 6694 S L17  
L41 11213 S GLYOXAL  
L42 528 S ETHANEDIAL  
L43 18 S GLYOXAZAL

L44 36 S GLYOXYLALDEHYDE  
L45 12111 S L40-L44  
L46 33 S L30  
L47 61 S L16  
L48 4 S L45 AND L47  
L49 2 S L46 AND L47  
L50 2 S L48 AND L49  
L51 5 S L16 (L) PREP+NT/RL  
L52 3 S L51 AND L45,L46  
L53 1 S L1 AND L47  
L54 3 S L52,L53  
L55 0 S L54 AND L31,L34,L27  
L56 0 S L54 AND L20-L23  
L57 0 S L54 AND L27  
L58 2 S L37  
L59 0 S L37(L) PREP/RL  
L60 8 S L10,L54,L58,L51  
L61 3 S L60 AND (PY<=2002 OR PRY<=2002 OR AY<=2002)  
L62 4 S L10,L61

FILE 'HCAPLUS' ENTERED AT 15:43:53 ON 24 MAR 2005

FILE 'CASREACT' ENTERED AT 15:44:41 ON 24 MAR 2005

L63 STR  
L64 0 S L63  
L65 STR L63  
L66 8 S L65  
L67 STR L63  
L68 5 S L67  
L69 98 S L67 FUL  
SAV L69 SHIAO653/A  
L70 23 S L69 AND L20-L23  
L71 21 S L70 AND L27  
L72 STR L67  
L73 96 S L72 FUL SUB=L69  
SAV L73 SHIAO653A/A  
L74 23 S L73 AND L70  
L75 6 S L74 AND (IMIDAZOL? OR DIARYLIMID?)/TI  
L76 4 S L75 NOT (OXALA? OR OXALIC?)/TI  
L77 4 S L76 AND L70,L71,L74

FILE 'CASREACT' ENTERED AT 15:53:29 ON 24 MAR 2005

=>